

OLED Encapsulation by Room Temperature Plasma-Assisted ALD Al₂O₃ Films

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8:40am **TF2-TuM3 Functional and Conducting Polymer Thin Films by Vapor Deposition**, *K. Gleason*, Massachusetts Institute of Technology
INVITED

Polymers provide extraordinary opportunities for functionalizing surfaces and creating thin films for integration into flexible devices. Vapor deposition is the method of choice for polymers having limited solubility or if the object to be coated degrades or swells upon exposure to solvent. Indeed, fluoropolymers, cross-linked materials, and electrically conducting polymers are three examples of organic materials which having little if any solubility, but which have been successfully deposited by two new vapor phase methods: initiated chemical vapor deposition (iCVD) and oxidative chemical vapor deposition (oCVD). By depositing polymers from the vapor phase, many wetting and solution effects are avoided, and conformal films can be created. The iCVD method is a platform technology which has produced more than 40 different homopolymers. Random copolymers, alternating copolymers, and grafted polymer chains have all been demonstrated using the iCVD method. Surface properties achieved include non-leaching antimicrobial layers, flexible dielectrics with low leakage current, and coatings with specific ligand binding capability on porous substrates and particles, superhydrophobicity, and superhydrophilicity. Engineering of iCVD coatings has led to extremely stable and flexible biopassivation coatings for neural implants, reversible swellable hydrogel layers, and enteric coatings of drug particles for pH sensitive release. Mechanistic understanding of the oCVD growth mechanism led to the ability to propagate conductive polymer chains directly from the growth surface with the use of any additional linker molecules. The creation of durable covalent linkages between the substrate and the surface functionalization layer affords excellent adhesion and also enables 60 nm lithographic pattern formation. The demonstration of patterns in conducting polymer patterns grafted onto common plastic substrates is a potential breakthrough for integrated circuitry for flexible electronics where mechanical robustness is extremely important, requiring excellent interfacial properties and adhesion. Each organic thin film synthesized by iCVD and oCVD displays a well-defined chemical structure as a result of selectively limiting the reaction pathways available during processing through a judicious choice of reactants and minimizing the energy input that drives the CVD chemistry. The exquisite control over composition and conformality achieved by these new vapor phase methods enables precise organic functionality to be designed and applied to almost any type of substrate. The fundamental understanding of the processes accelerates both discovery of and scale-up.

9:20am **TF2-TuM5 CVD of Three Aminosilanes on Silicon Oxide: Effect of Silane Concentration, Surface Characterization and Stability, and Cyanine Dye Adsorption**, *M.R. Linford, F. Zhang*, Brigham Young University, *H. Samha*, Southern Utah University, *K. Sautter*, Yield Engineering Systems, *R.C. Davis*, Brigham Young University

Amino silanes are among the most frequently deposited reagents for surface modification to prepare biosensors and other biologically active materials. Of the various ways to deposit silanes, it is becoming increasingly recognized that CVD is the most reproducible and reliable. However, CVD of these important reagents is also much less studied than the less reproducible and much more widely practiced deposition from solution. We also stress the environmentally friendly and industrially viable nature of CVD silane deposition. Our work differs from that of most academic researchers because of the tool we use for silane deposition, which is a commercially available CVD system (the 1224P) from Yield Engineering Systems. This tool gives complete control of oven temperature, pressure, and reagent delivery, in addition to offering plasma pretreatment of the substrates at a range of powers and conditions. In our work we have explored the CVD at 150°C of 3-aminopropyltriethoxysilane (APTES), which is arguably the most widely used and important silane. We show that surface saturation leading to the same level of surface functionalization occurs over a very wide range of gas phase concentrations. This important result indicates that there is a wide process window for APTES deposition. We further compare CVD of APTES to the gas phase deposition of two of its aminosilane analogs – one with two methyl groups (3-aminopropyltrimethylsilane), and the other with two isopropyl groups (3-aminopropyl-diisopropylethoxysilane). X-ray photoelectron spectroscopy (XPS) shows a decrease in nitrogen concentration for these two molecules compared to APTES. All of these films are extremely flat by atomic force microscopy, and spectroscopic ellipsometry indicates the expected monolayer coverages of our silanes. Of particular significance is the stability against base of the diisopropyl aminosilane, which should make it valuable in a number of applications. The interactions of our different amino surfaces with a cyanine dye are also probed, and the structure/adsorption of the dye seems to be well correlated to the amine density determined by XPS.

9:40am **TF2-TuM6 Novel Precursors for CVD of Amorphous and Crystalline Cobalt Group Metal-Phosphide Films**, *J. Rivers, R. Jones*, The University of Texas at Austin

Volatile Cobalt group complexes were synthesized as single-source precursors for chemical vapor deposition of amorphous and crystalline metal-phosphide thin films. Phosphide alloys of transition metals are of interest due to their use as barriers against corrosion, electrodes, batteries, catalysts, and as diffusion barrier layers in integrated circuits. Volatile precursors allow use of CVD which is advantageous to other physical methods such as PVD. Precursors were specifically designed and synthesized utilizing ligands which impart volatility such as 3,5-bis(trifluoromethyl)pyrazole and trimethylphosphine. Complexes studied include $[\text{Rh}((\text{CF}_3)_2\text{-Pz})(\text{PMe}_3)_3]$, $[\text{Co}(\text{PMe}_3)_4]$, $[\text{Co}((\text{CF}_3)_2\text{-Pz})(\text{PMe}_3)_3]$, and $[\text{Co}((\text{CF}_3)_2\text{-Pz})_2(\text{PMe}_3)][\text{CoH}(\text{PMe}_3)_4]$. The nature of the films depends on reactor conditions such as flow rate, deposition time, substrate temperature, and annealing conditions. Films were grown at temperatures under 400 °C in a hot-wall reactor utilizing dynamic vacuum or Ar as a carrier gas and characterized using XPS, XRD, and SEM.

10:40am **TF2-TuM9 Kinetic Study on InGaAsP-MOCVD Using Selective Area Growth and its Application to OEIC Device Fabrication**, *Y. Shimogaki*, The University of Tokyo, Japan
INVITED

Metal-organic chemical vapor deposition (MOCVD) is a well developed deposition technology for the fabrication of InGaAsP compound semiconductors. If the substrate is partially covered by dielectric masks such as SiO₂, selective growth will occur and no growth takes place on the mask during the MOCVD. Then reactants will be accumulated above the mask area and migrate towards the adjacent non-mask covered area, causing growth rate enhancement. This growth rate enhancement will be proportional to the size of the mask, because larger mask will accumulate more reactants. Thus we can control the selective growth rate by the area of the mask. This technique is called selective area growth (SAG). The thickness, composition, and even the properties of the SAG-epitaxial layers can be locally tailored by specifically designed mask patterns. For example, in the single-step growth of multiple-quantum-well structures (MQWs) on well-designed mask patterns, it is possible to control the effective band gap energy of the layers by changing the well width and composition. Thus, passive and active devices can be locally integrated simultaneously by designing the mask size and pattern. This technology will reduce the cost of fabrication and enhances production yield of opto-electronic integrated circuit (OEIC).

Numerical simulation on growth rate non-uniformity of SAG in sub-millimeter scale can extract real surface kinetics in MOCVD process for InGaAsP-compounds, which is normally hindered by mass transport rate of film precursors [1]. SAG analysis with non-linear surface kinetics is introduced for the first time to analyze group-III precursor partial pressure dependency of InGaAsP-MOCVD [2]. Important kinetic parameters, such as surface reaction rate constant, adsorption equilibrium constant, and surface coverage, have been extracted. Such non-linear kinetic analysis using SAG (micro analysis) is combined with computational fluid dynamics (CFD) reactor-scale analysis (macro analysis) to elucidate the main reaction mechanism of InGaAsP-MOCVD process in the whole reactor. The design of photo-luminescence (PL) wave length for optical device by tailoring the mask pattern will be demonstrated.

References

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2. Y. Wang, H. Song, M. Sugiyama, Y. Nakano, and Y. Shimogaki, *Jpn. J. Appl. Phys.*, **48** (2009) 041102.

11:20am **TF2-TuM11 OLED Encapsulation by Room Temperature Plasma-Assisted ALD Al₂O₃ Films**, *W. Keuning, M. Creator, E. Langereis*, Eindhoven University of Technology, Netherlands, *H. Lifka, P. van de Weijer*, Philips Research Laboratories, Netherlands, *M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Organic light emitting diodes (OLEDs), both small molecule and polymer LEDs) require excellent gas and moisture permeation barrier layers to increase their lifetime. The quality of the barrier layer is ultimately controlled by the presence of defects in the layer. Although a barrier layer may be intrinsically excellent (water vapor transmission rate, WVTR $\leq 10^{-6}$ g·m⁻²·day⁻¹) the protected device may fail in the presence of defects that lead to preferential diffusion pathways for H₂O (e.g., defects caused by particles from the environment and/or production process). The state-of-the-art barrier coatings are micrometer-thick multi-layer structure, in which organic interlayers are alternated with inorganic barrier layers with the purpose of decoupling the above-mentioned defects. Recently, atomic layer deposition (ALD) has been successfully tested for the deposition of very thin (< 50 nm) single layer permeation barriers on pristine polymer

substrates [1,2], showing the potential of this highly uniform and conformal deposition technique in the field of moisture permeation barriers. In this contribution the encapsulation of OLEDs by plasma-assisted ALD of thin (20-40 nm) Al₂O₃ layers is addressed. The layers are synthesized at room temperature by sequentially exposing the substrate to Al(CH₃)₃ vapor and a remote inductively coupled O₂ plasma in Oxford Instruments FlexAL™ and OpAL™ reactors. The intrinsic quality of the deposited ALD layers was determined by monitoring the oxidation of a Ca film encapsulated by the Al₂O₃ film: WVTR values as low as 2·10⁻⁶ g·m⁻²·day⁻¹ have been measured. The potential of ALD layers in encapsulating OLEDs, and therefore in successfully covering the defects present on the device, has been investigated by means of electroluminescence measurements of polymer-LEDs (effective emitting area of 5.8 cm²). The black spot density and area growth were followed as a function of the time under standard conditions of 20°C and 50% relative humidity. Within a 500 h test ALD-encapsulated OLEDs show approximately half the black spot density compared to devices encapsulated by plasma deposited a-SiN_x:H (300 nm thick). The black spot density is further reduced by combining the a-SiN_x:H and ALD Al₂O₃ layers. These results point towards a very promising application of ALD Al₂O₃ layers in the field of OLED encapsulation and will be interpreted in terms of possible mechanisms related to film growth in multi-layer structures.

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11:40am **TF2-TuM12 Controlled Doping of CVD Diamond with Mid-to-High Z Metals**, *M.M. Biener, J. Biener*, Lawrence Livermore National Laboratory, *H. Obloh*, Fraunhofer-Institut für Angewandte Festkörperphysik, Germany, *S.O. Kucheyev, Y.M. Wang*, Lawrence Livermore National Laboratory, *W. Mueller-Sebert*, Fraunhofer-Institut für Angewandte Festkörperphysik, Germany, *B.S. El-Dasher*, Lawrence Livermore National Laboratory, *A. Kriele*, Fraunhofer-Institut für Angewandte Festkörperphysik, Germany, *N.E. Teslich Jr.*, Lawrence Livermore National Laboratory, *C. Wild*, Fraunhofer-Institut für Angewandte Festkörperphysik, Germany, *A.V. Hamza*, Lawrence Livermore National Laboratory

The development of diamond chemical vapor deposition (CVD) techniques has led to numerous thin film applications. Besides grain boundary engineering, doping is one way to further optimize diamond's unique materials properties for a given application. Here, we report on controlled doping of synthetic diamond with Mo and W by adding volatile metal precursors to the diamond CVD growth process. Effects of deposition temperature, grain structure and precursor exposure on the doping level are systematically studied. The metal atoms are uniformly distributed throughout the CVD diamond film, and doping levels of up to 0.25 at.% have been achieved. Rutherford backscattering/ channeling experiments reveal that the metal atoms do not occupy substitutional or interstitial sites, thus suggesting the formation of more complex sites such as metal-vacancy clusters.

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